Chloride

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Chloride

* Chloride, in the form of the Cl^- ion,
* one of the major inorganic *anions* in saltwater and freshwater.
* It originates from the dissociation of salts, such as sodium chloride or calcium chloride, in water.

$$NaCl(s) \text{ ----> } Na^+(aq) + Cl^-(aq)$$

$$CaCl_2(s) \text{ ----> } Ca^{2+}(aq) + 2\ Cl^-(aq)$$

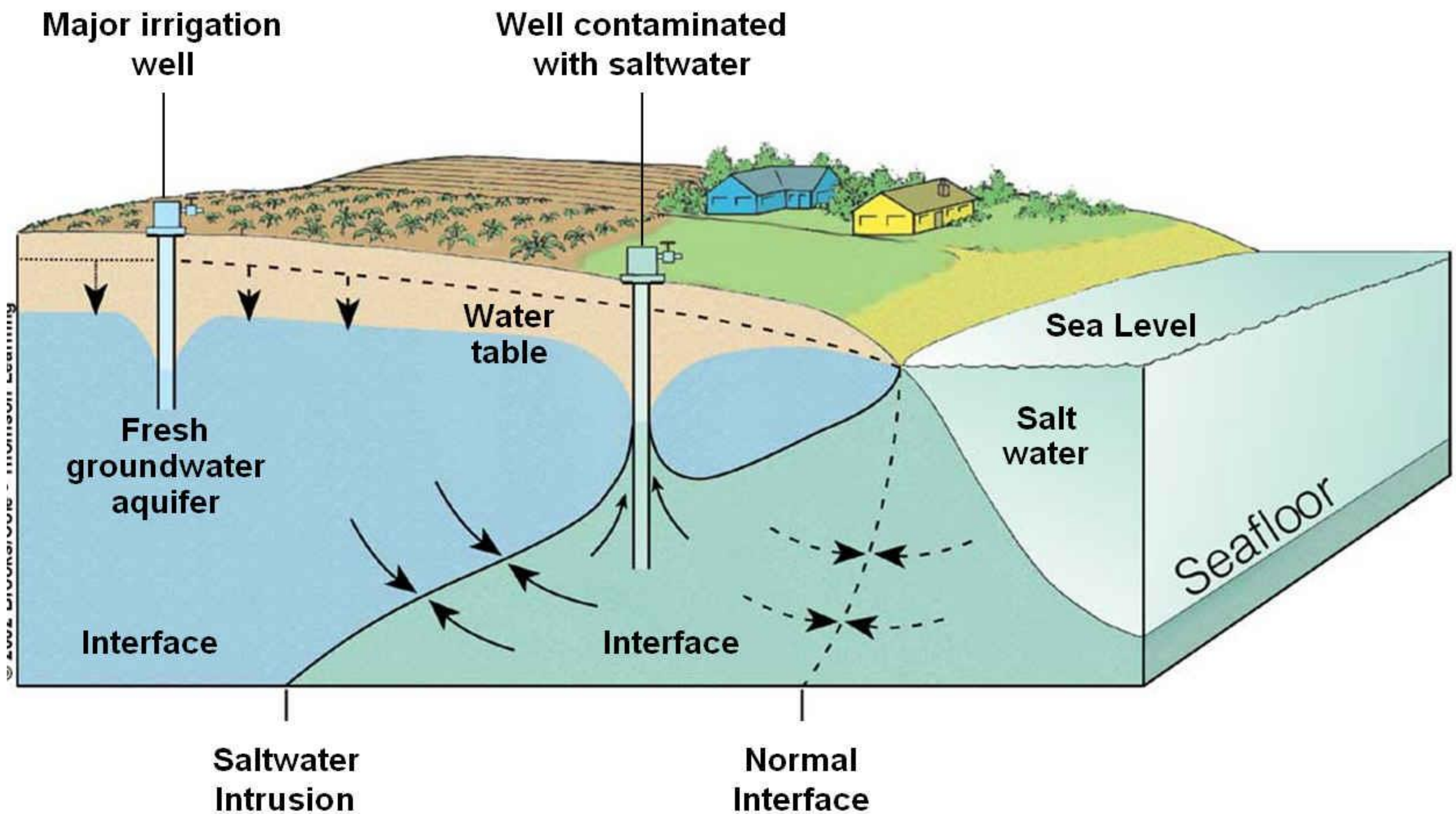
Chloride

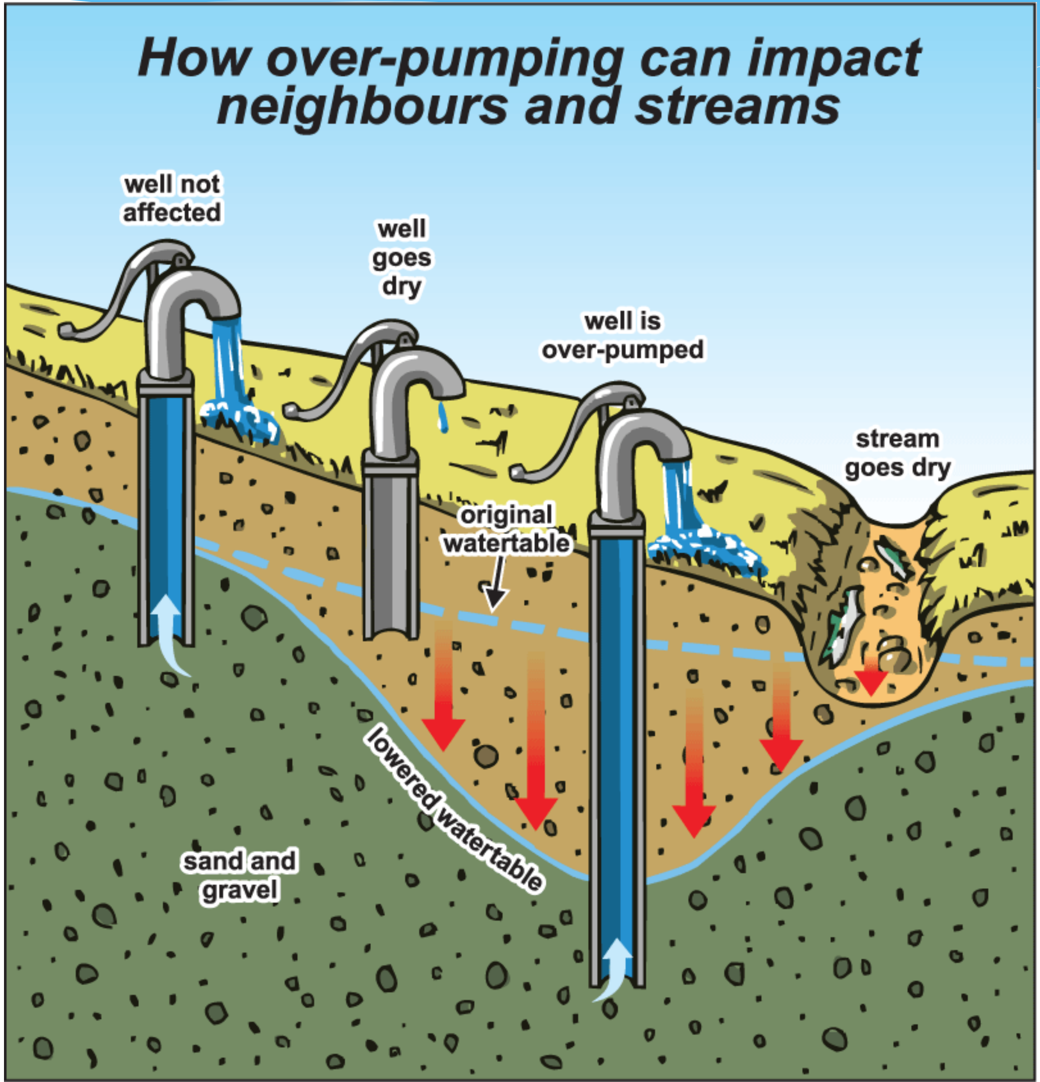
* Variable concentrations in natural water sources
  * Low $[Cl^-]$ → upland and mountain supplies
  * High $[Cl^-]$ → river and groundwaters
  * Very high $[Cl^-]$ → Sea and ocean waters
* As mineral content ↗ → chloride content ↗

Sources of Chloride

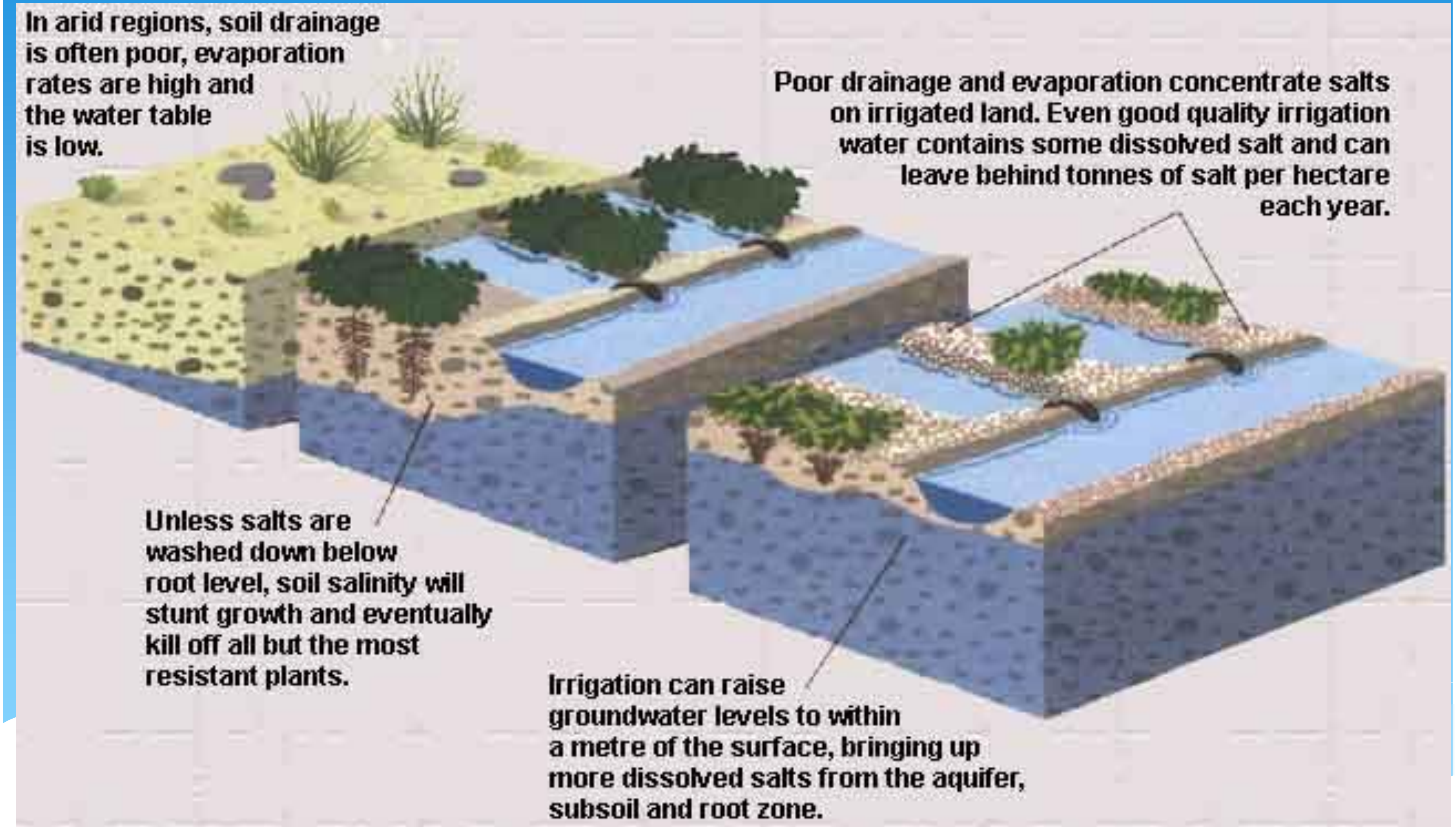
* Surface waters dissolve chlorides from top soil.
* Spray from the ocean is carried in land as droplets or flooding.
* Ocean and sea waters invade the rivers that drain into them.
* Intermixing between freshwater and saltwater layers

Salt water intrusion




How over-pumping can impact neighbours and streams
well not affected
well goes dry
well is over-pumped
stream goes dry
original watertable
lowered watertable
sand and gravel

How saline water reaches the crops:



Chloride in wastewater

- Human urine contain chloride → originating from consumed food and water

  6 gr Cl^- / person / day

- This increases the amount of Cl- in municipal wastewater about 15 mg/L
- Many industrial wastes contain high amounts of chloride

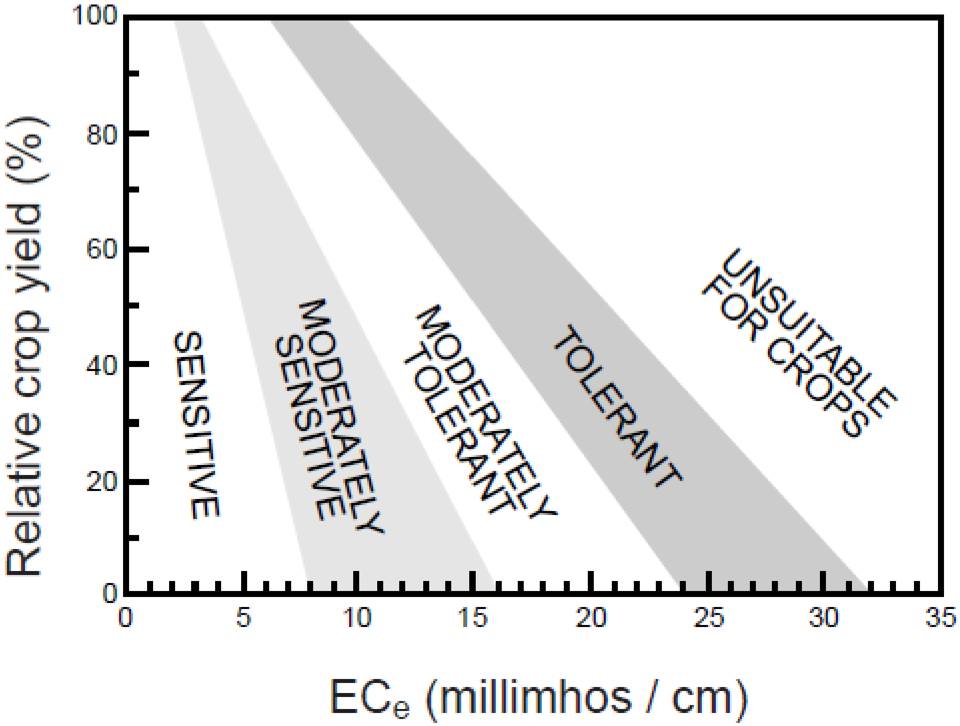
Significance of Chloride

- Not harmful to humans at reasonable concentrations
  - Conc. >250 mg/L → salty taste to water
- Secondary standard
  - EPA=250 mg/L
  - WHO=250 mg/L
  - Turkish standards=250 mg/L
- In regions where water is scarce, conc. as high as 2000 mg/L→ people get used to it.

How are salts harmful to plants

- CAUTION: Salinity is not only due to Cl-, but also due to other ions like Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, HCO_3^{-}
  - Osmotic influences
  - Specific ion toxicity

Key: Salinity tolerance zones



(adapted from Maas and Hoffman 1977).

Turkish Standards on Irrigation water

* Teknik Usuller Tebligi, 2010

Tablo E7.2 Sulama suyunun kimyasal kalitesinin değerlendirilmesi için geliştirilmiş tablo

Parametreler		Birimler	Kullanımında zarar derecesi: Yok (I. sınıf su)	Az – orta (II. sınıf su)	Tehlikeli (III. sınıf su)
Tuzluluk					
İletkenlik		µS/cm	< 700	700-3000	>3000
Toplam çözünmüş Madde		mg/L	< 500	500-2000	>2000
Geçirgenlik					
SAR_{Tad}	0-3	EC	≥ 0.7	0.7-0.2	< 0.2
	3-6		≥ 1.2	1.2-0.3	< 0.3
	6-12		≥ 1.9	1.9-0.5	< 0.5
	12-20		≥ 2.9	2.9-1.3	< 1.3
	20-40		≥ 5.0	5.0-2.9	< 2.9
Özgül iyon toksisitesi					
Sodyum (Na)					
Yüzey sulaması		mg/L	< 3	3-9	> 9
Damlatmalı sulama		mg/L	< 70	> 70	
Klorür (Cl)					
Yüzey sulaması		mg/L	< 140	140 –350	> 350
Damlatmalı sulama		mg/L	< 100	> 100	
Bor (B)		mg/L	< 0.7	0.7-3.0	> 3.0

Specific ion toxicity

Tablo E7.5 Bitkilerin yapraklarına zarar veren klorür konsantrasyonları

Hassaslık	Klorür konsantrasyonu, mg/L	Etkilenen bitki
Hassas	< 178	Badem, kayısı, erik
Orta hassas	178-355	Üzüm, biber, patates, domates
Orta toleranslı	355-710	Kaba yonca, arpa, mısır, salatalık
Toleranslı	> 710	Karnabahar, pamuk, susam, sorgum, şeker pancarı, ayçiçeği

Speicific ion toxicity of Chloride on plants

Heavily salted	
Salinity affects as much as one-quarter of the irrigated land in some countries:	
Country	**Percentage salinated**
Mexico	10
India	11
Pakistan	21
China	23
United states	28

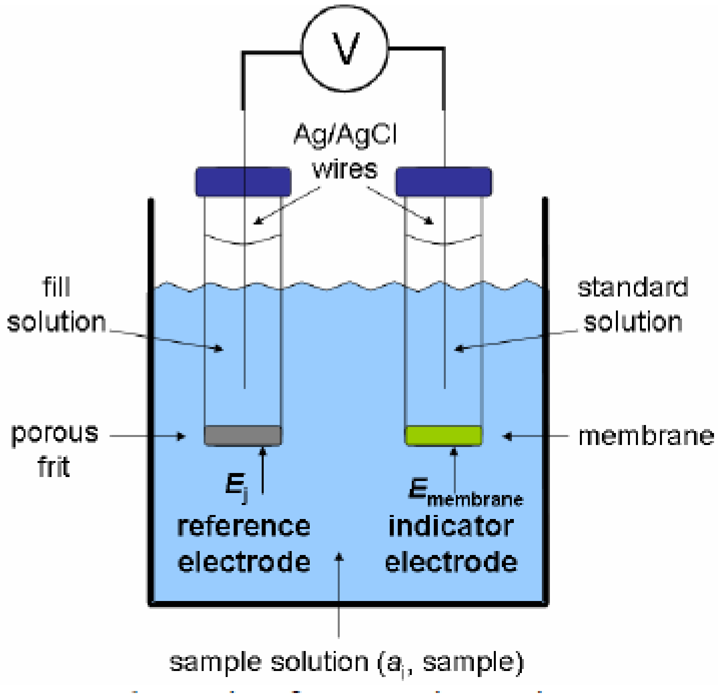
Methods of determination

* Argentometric Method
* Potentiometric procedure
  * Silver nitrate to form AgCl complex and employ a silver-silver chlorideelectrode system to detect the end point
* Mercuric Nitrate Method→reading assignment
* Ferricyanide Method
* Ion chromotography

Potentiomteric Procedure

- Inside of the tube is a reference solution, which contains a known and fixed concentration of analyte (Cl^-) solution.

- any change in measured potential is caused only by a change in potential across the membrane and is a function of the analyte chloride ion activity (or concentration).



Mohr (Argentometric) Method

- **Argentometry** is a type of titration involving the silver(I) ion
- Employs silver nitrate as the titrant

0.0141 N silver nitrate (N / 71) Each ml = 0.5 mg Cl^-

- Potassium chromate as the indicator
- Turns to reddish-brown at the endpoint

$$Cl^- \text{ (in mg/L)} = \frac{(\text{mL } AgNO_3 - \text{blank}) \times 0.5 \times 1000}{\text{mL sample}}$$

since $0.0141 \times 35.45 = 0.5$.

Processes occuring…

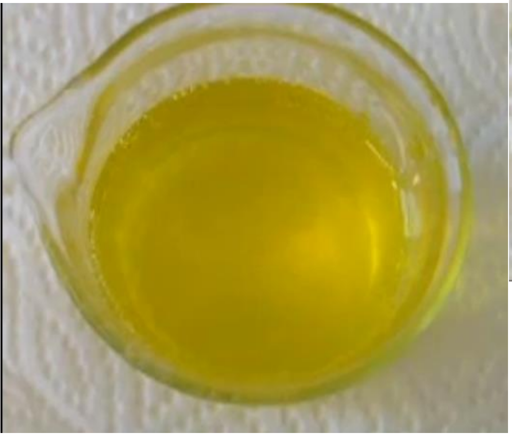
Ex: $Ag^+ + Cl^- \rightleftharpoons \underset{\text{white}}{AgCl(s)}$

– At chemical equivalence:

$$[Ag^+] = \sqrt{K_{sp}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}\ M$$

– And $2\,Ag^+ + CrO_4^{2-} \rightleftharpoons \underset{\text{red}}{Ag_2CrO_4(s)}$

$$[CrO_4^{2-}] = \frac{K_{sp}}{[Ag^+]^2} = \frac{1.2 \times 10^{-12}}{(1.35 \times 10^{-5})^2} = 6.6 \times 10^{-3}\ M$$



Mohr Method

1. A uniform sample size must be used, preferably 100 mL, so that ionic concentrations needed to indicate the end point will be constant.
2. The pH must be in the range of 7 to 8 because Ag^+ is precipitated as $AgOH(s)$ at high pH levels and the CrO_4^{2-} is converted to $Cr_2O_7^{2-}$ at low pH levels.
3. A definite amount of indicator must be used to provide a certain concentration of CrO_4^{2-}; otherwise $Ag_2CrO_4(s)$ may form too soon or not soon enough.

Sample problem

100.0 mL of waste water is titrated using the Mohr method. A chromate endpoint is reached after addition of 16.43 mL of 0.09762 M $AgNO_3$. What is the chloride concentration in mg Cl^-/L?

Solution

The Mohr titration has 1:1 stoichiometry

$M_1V_1 = M_2V_2$

M_1 (100.0 mL) = (0.09762 M) (16.43 mL)

M_1 = 0.01604 M Cl^-

$$\frac{0.01604 \text{ moles } Cl^-}{1 \text{ L solution}} * \frac{35.453 \text{ g } Cl^-}{\text{mole } Cl^-} * \frac{1000 \text{ mg}}{1 \text{ g}}$$

= 568.6 mg/L

(which is actually pretty high – anything above 250 mg/L will taste salty)

Application of Chloride data

* Interferes with the measurement of COD
* Used as a tracer